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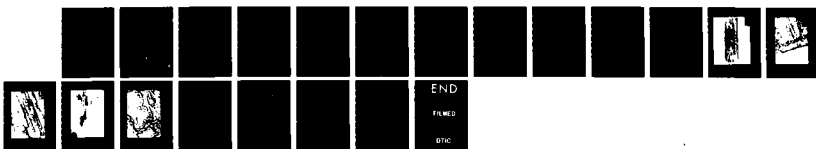
THE CORROSION BEHAVIOR OF A GRAPHITE FIBER/MAGNESIUM
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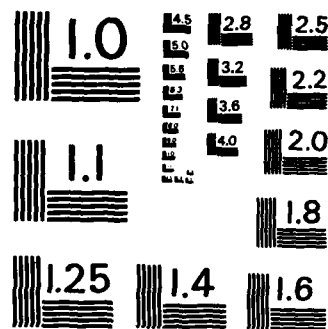
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The Corrosion Behavior of a Graphite Fiber/Magnesium Metal Matrix Composite in Aqueous Chloride Solution

P. P. TRZASKOMA

*Environmental Effects Branch
Material Science and Technology Division*

AD-A159 121

September 19, 1985

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NAVAL RESEARCH LABORATORY
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THE CORROSION BEHAVIOR OF A GRAPHITE FIBER/MAGNESIUM METAL MATRIX COMPOSITE IN AQUEOUS CHLORIDE SOLUTION

Introduction

High unidirectional strength-to-density ratios combined with low coefficients of thermal expansion make graphite fiber/magnesium composites attractive for use in space applications. Currently various laboratories are preparing and testing these materials in order to define the design, composition, and fabrication techniques that optimize desirable physical properties. Along with these developments it is also important to evaluate corrosion behavior in aqueous environments.

Background

It is well known that magnesium is one of the most chemically active metals. It dissolves readily in water, producing magnesium hydroxide and hydrogen gas (1). Although the rate and extent of this reaction depends on several environmental factors; presence of oxygen, type and concentration of anions, and temperature, it is crucially dependent upon pH and alloy composition and purity.

Robinson's work in 1946 summarizes the effect of pH on magnesium corrosion (2). At low pH values (below 9.5) where conditions do not favor the formation of anodic films, dissolution of the metal is uniform and controlled by the rate of hydrogen discharge. At higher pH values (above 10.5) protective films are established on the metal and the rate of general attack decreases with increasing pH. Corrosion tends to be more localized. In the pH range of 9.5 - 10.5 electrolyte characteristics rather than pH control the type of attack and dissolution rate.

The effect of alloy composition and purity on magnesium corrosion was studied extensively by Hanawalt and co-workers in 1942 (3). The purpose of this work was to explain the disproportionate difference in the corrosion rates of commercially pure magnesium (99.9% pure), (5-100 mg/cm²-day) and high purity magnesium (0.15 ± 0.05 mg/cm²-day) in 3% NaCl solution. By varying the concentration of several elements in combination with magnesium, it was found that the type and concentration of some elements have a profound influence on corrosion rates. In the case of iron, copper, and nickel for example, a critical concentration exists above which the corrosion of magnesium increases precipitously. The role of these elements according to Hanawalt is to provide low over-voltage sites for hydrogen evolution and thereby increase the cathodic reaction rate. Since the cathodic reaction is rate determining the overall corrosion rate also increases.

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Although it has been shown that chloride increases the corrosion rate of magnesium in water, the exact function of this ion is not yet understood (4,5). Experimental evidence does indicate, however, that chloride is active in the anodic corrosion reaction and probably interferes with the formation of protective films (6,7).

Because of the very reactive nature of magnesium and its propensity to galvanic corrosion, the corrosion performance of graphite fiber/magnesium composite materials during exposure to marine or moist atmospheric conditions is of great concern. Galvanic coupling of the composite constituents together with the naturally high corrosion rates of magnesium alloys could result in rapid, catastrophic failure of these materials during storage, working and transportation.

In this work the corrosion behavior of a graphite fiber/magnesium composite is studied in aerated, dilute chloride solutions at near neutral pH. The purpose is to determine the effect of graphite on the corrosion characteristics of the magnesium matrix, and to provide information that can be used in fabrication to minimize corrosion.

Experimental

Materials and Sample Preparation

Composite specimens were prepared by Amercom Inc., Chatsworth, CA. Graphite fibers (100 pitch, 10 μ m in diameter) were coated with molten TiB and then molten magnesium alloy AZ91C. The wires thus prepared were hot pressed between foils of magnesium alloy AZ31B. The thickness of the outer foils (face plates) is 0.20 mm and the thickness of the entire composite is 0.84 mm. The composite consists of 26.5 volume per cent graphite. Figure 1 shows a schematic drawing of the composite material.

Pure samples (no graphite) of magnesium alloys AZ31B and AZ91XD were also used for various tests. These materials were obtained from Dow Chemical U.S.A., Freeport, Texas and the nominal compositions are given in Table I.

TABLE I

Nominal Composition of Magnesium Alloys

	Al%	Zn%	Mn%	Si%	Cu%	Ni%	Fe%	Others % (Maximum)
AZ31B ¹	2.5-3.5	0.7-1.3	0.02	0.05	0.01	0.0010	0.002	
AZ91XD ¹	8.5-9.5	0.5-0.9	0.15	0.02	0.015	0.001	0.005	0.011
AZ91C ²	8.1-9.3	0.4-1.0	0.13	0.30	0.10	0.01		0.30

¹ Dow Chemical Designation

² ASTM Designation

Graphite specimens used in the electrochemical tests were P-55 "Thornel" carbon fiber grade VSB-32. This material is supplied in strands containing 2000 filaments per strand and each filament has a diameter of 10 μm .

Specimens for immersion were cut into coupons approximately 2.8 cm x 1.05 cm, cleaned with detergent, rinsed several times with distilled water, and ultrasonically cleaned with several rinses of ethanol. The samples were then left in a desiccator until the tests were started (at least 24 hours).

For the electrochemical measurements magnesium and composite specimens were cut into discs ($d = 1.5$ cm), ground up to 600 grit SiC paper, ultrasonically cleaned with several rinses of ethanol, and placed in a PAR flat specimen holder. The area of exposed sample was about 1.0 cm^2 .

Graphite electrodes were prepared by attaching a strand of graphite approximately 1.0 cm in length to copper wire using a solderless connector. The junction and wire were encased in glass tubing and the mouth of this tubing, near the graphite strand, was sealed with quick drying epoxy. Before immersion, the epoxy was covered with two coatings of glyptol. The graphite strand was trimmed to a desired length and the exposed surface area is easily calculated from the length of the strand and the diameter and number of filaments per strand.

Solutions were prepared from Fisher certified reagents dissolved in distilled water from a Barnstead still.

Procedures

For the immersion tests composite coupons were suspended by PTFE thread and immersed in a beaker containing about 175 mls of 0.001 N NaCl ($\text{pH} = 5.24$) solution. Tests were run at room temperature with the beakers open to the air. After 5 days the samples were removed from solution, cleaned by immersing in boiling chromic acid solution for one minute, rinsed in distilled water, air dried and observed in the SEM. The chromic acid cleaning solution was 1% AgCrO_4 and 15% CrO_3 dissolved in water.

Two types of electrochemical tests were run in this study: (1) open-circuit potential-time measurements and (2) galvanic current measurements. Tests were run in a PAR electrochemical cell using a saturated calomel reference electrode. The electrolyte was a borated boric acid buffer solution containing 1000 ppm NaCl (0.0171 N) and had a pH of 8.4. Solutions were aerated and stirred by bubbling with breathing air at least 12 hours prior to and during the potential-time tests. For the galvanic current measurements the cell was aerated for 12 hours bubbling was then stopped, the cell closed, and tests run without stirring.

Potential-time measurements were obtained by immersing samples in solution and monitoring the open-circuit potential up to 22 hours on a Keithly electrometer and strip chart recorder.

For the galvanic current measurements separate magnesium alloy (AZ31B) and graphite electrodes were simultaneously immersed in solution until each attained a steady potential. This took about 2 hours. The electrodes were then coupled through a potentiostat and, using it as a zero resistance ammeter, the short-circuit current was measured. This current was monitored continuously until a steady value was maintained for about one hour. The steady current was interpreted to be the galvanic short-circuit current between the magnesium alloy and graphite fiber. Keeping the surface area of magnesium constant (approximately 1 cm^2) the experiment was repeated with various lengths of graphite strands. In this way it was possible to vary the surface area ratios of graphite (surface area of graphite:total surface area) and study the effect of the exposed surface area of fiber on the galvanic currents. This technique of modeling the composite to determine short-circuit currents between the constituents has been described in the literature (8). Approximately 650 mls of solution were used for each test.

Results and Discussion

Immersion Tests

When composite samples are immersed in 0.001N NaCl rapid hydrogen evolution is immediately observed over the entire surface of the material. Within a few hours a gray film develops and gas evolution is somewhat diminished. Within five days severe localized attack is observed at the edges of the sample where there are exposed graphite fibers. Figures 2-6 show various features of a sample after the immersion test.

Figure 2 illustrates severe corrosion at the edges of the specimen. In this micrograph the graphite fibers lie vertically in the plane of the paper. Figure 3 is a magnification of a sample edge and shows exposed graphite fibers, a thin strip of remaining foil sheet (AZ31B) and an area (right) in which the foil has completely dissolved exposing graphite fibers and the underlying magnesium alloy (AZ91C). Figure 4, a further magnification of this area, shows bare graphite fibers and attack of AZ91C. Figure 5 shows an area in which several graphite fibers have been broken, possibly during the corrosion process. Figure 6 is a micrograph of an interior area of the material. In this region attack is not as severe and seems to follow grain boundaries.

Thus after a very short period of immersion in dilute chloride solution there is considerable degradation of the composite, especially in regions containing exposed graphite. Within five days there is penetration of the face plate, attack of the underlying matrix material and damage to the graphite fibers. Although interior attack is not as severe it is still apparent and gives the specimen an etched appearance.

Electrochemical Tests

To better understand the role of graphite in the corrosion of the composite, several electrochemical tests were run in a borated boric acid buffer solution containing a low concentration of chloride (pH = 8.4, 1000 ppm NaCl). Figure 7 shows the open-circuit potentials of the composite, two magnesium alloys, and graphite as a function of time in the buffer solution. For both alloys and the composite the potential initially drifts in the positive direction, but after two hours it reaches a steady value with time. While the potential is equilibrating, an incomplete, black film develops on the metal surface. With the appearance of this film, the hydrogen evolution rate decreases. The steady potentials of both alloys and composite are virtually the same (about -1.64V). This result is expected for the composite since under the experimental conditions there are no exposed graphite fibers and the specimen is simply an AZ31B surface. The black film is easily removed from the specimens by ultrasonic cleaning in water and the underlying material has an etched appearance.

The open-circuit potential of graphite also becomes stable in about two hours and the value, -0.325V, is about 1.3 volts more anodic than the magnesium metals. No visible changes are observed on the graphite.

The large potential difference between the graphite and magnesium alloys suggests that galvanic interactions should take place on the composite in regions where the magnesium and graphite are both exposed to solution. In the galvanic current tests significant short-circuit currents were measured when graphite was coupled to AZ31B. Figure 8 shows these currents as a function of time for various surface area ratios of graphite. Initially the current varies with time but becomes steady after two to four hours. This steady current is taken as the galvanic current of the couple. As the surface area ratio of graphite increases the galvanic current increases. During these experiments gas evolution is observed on both the graphite fibers and magnesium alloy.

The potential of the various couples versus a reference electrode is also shown in Figure 8. This potential is analogous to the open-circuit potential of a graphite/magnesium composite having the same exposed surface area of graphite. The open-circuit potentials are about the same for all couples and about 100 mV more positive than that of the alloy alone. (In one case at a surface area ratio of 0.28, the potential of the couple was unusually negative. In this case the potential of the alloy specimen before coupling also had an unusually negative value.) The positive shift in potential is due to the fact that graphite provides an alternative or additional site for the cathodic reaction (oxygen reduction and/or hydrogen evolution); as a result, the overall cathodic reaction rate increases and the corrosion potential shifts in the positive direction. While differences in open-circuit potential might be expected for the various couples, (i.e. more positive potentials as the surface area of graphite increases) it is not surprising that this is not observed for the magnesium system. Because magnesium has a very low anodic polarizability, large changes in the cathodic reaction rate have only small effects on the mixed or open-circuit potential.

Figure 9 is a plot of galvanic current versus surface area ratio of graphite. Although the exact contribution of galvanic corrosion to the total corrosion rate of the composite has not been determined, it is possible, using Faraday's Laws and this curve, to calculate the corrosion rate due to galvanic corrosion as a function of the surface area ratio of graphite. When 10% of the composite surface is graphite for example, the galvanic corrosion rate in the chloride solution of the borated buffer is $1.8 \text{ mg/cm}^2\text{-day}$ (0.15 ipy). This value alone is about 3% the minimum acceptable value for corrosion of structural materials as suggested in the literature (9).

Thus it has been shown that in the presence of aqueous chloride environments the corrosion of graphite/magnesium is extremely rapid and that the presence of exposed graphite fibers accelerate this attack by galvanic coupling.

Summary

1. The corrosion rate of the graphite fiber/magnesium composite is extremely rapid in dilute chloride solution. Within five days exposure to 0.001 N NaCl there is severe degradation of the material including dissolution of the face plate, attack of the underlying metal, and damage to the fibers.
2. Corrosion is a result of both rapid reaction of magnesium with water and galvanic coupling between the graphite fibers and matrix alloy. When 10% of the composite surface is graphite, the galvanic corrosion rate in dilute chloride ($1.8 \text{ mg/cm}^2 \text{ day}$) exceeds the minimal acceptable value of corrosion for structural materials. As the volume ratio of graphite increases the corrosion rate increases.
3. Two factors must be considered in order to alleviate the corrosion problem. Improvement of the general corrosion behavior of the constituent metal alloys and elimination of the exposed graphite fibers.

Acknowledgment

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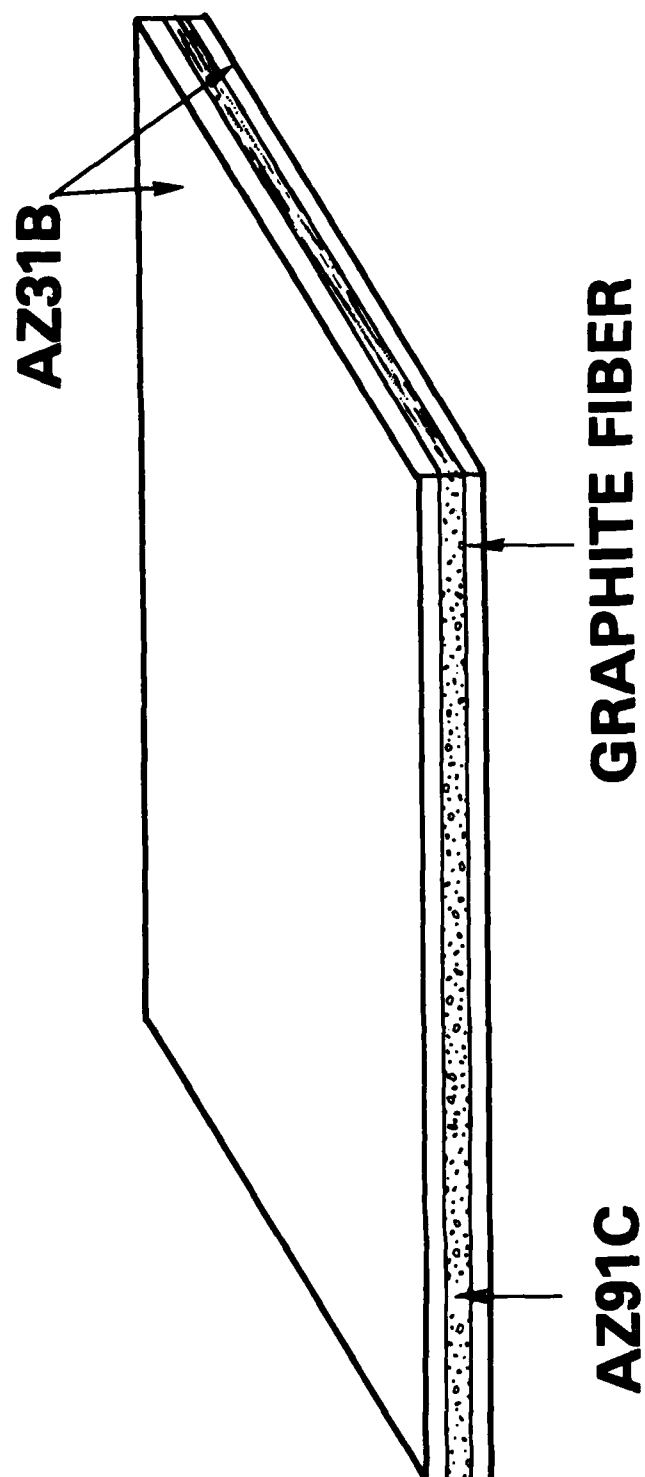


Fig. 1 — Schematic drawing of the graphite fiber/magnesium composite.

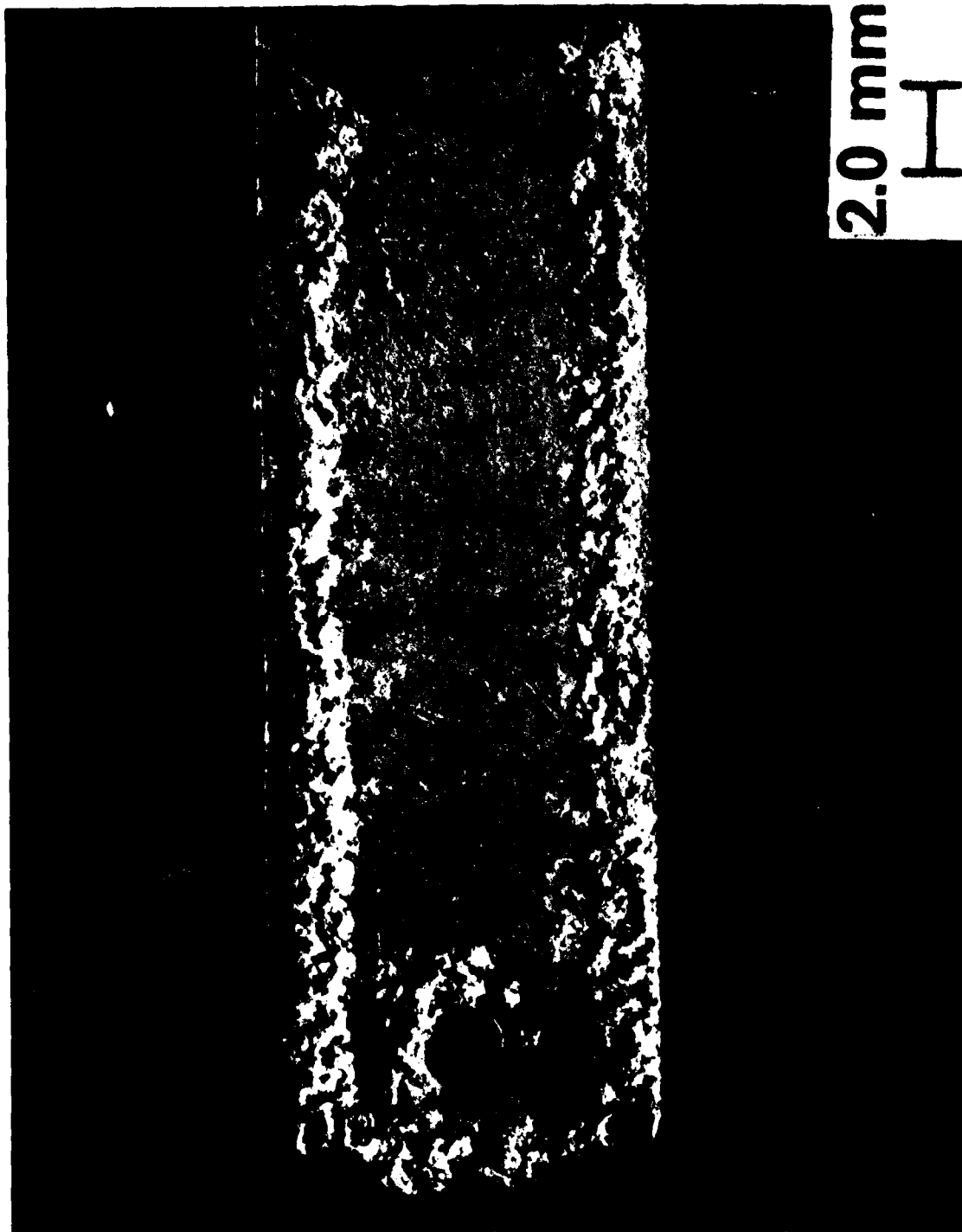


Fig. 2 — Graphite fiber/magnesium composite after immersion
in 0.001 N NaCl for five days.



Fig. 3 — View of graphite fiber/magnesium composite after immersion in 0.001 N NaCl showing edge attack and exposure of graphite fibers.



Fig. 4 — View of graphite fiber/magnesium composite after immersion in 0.001 N NaCl showing bare graphite fibers and attack of AZ91C.



Fig. 5 — View of graphite fiber/magnesium composite after immersion
in 0.001 N NaCl showing broken graphite fibers.



Fig. 6 — View of interior region of graphite fiber/magnesium composite after immersion in 0.001 N NaCl showing corrosion morphology.

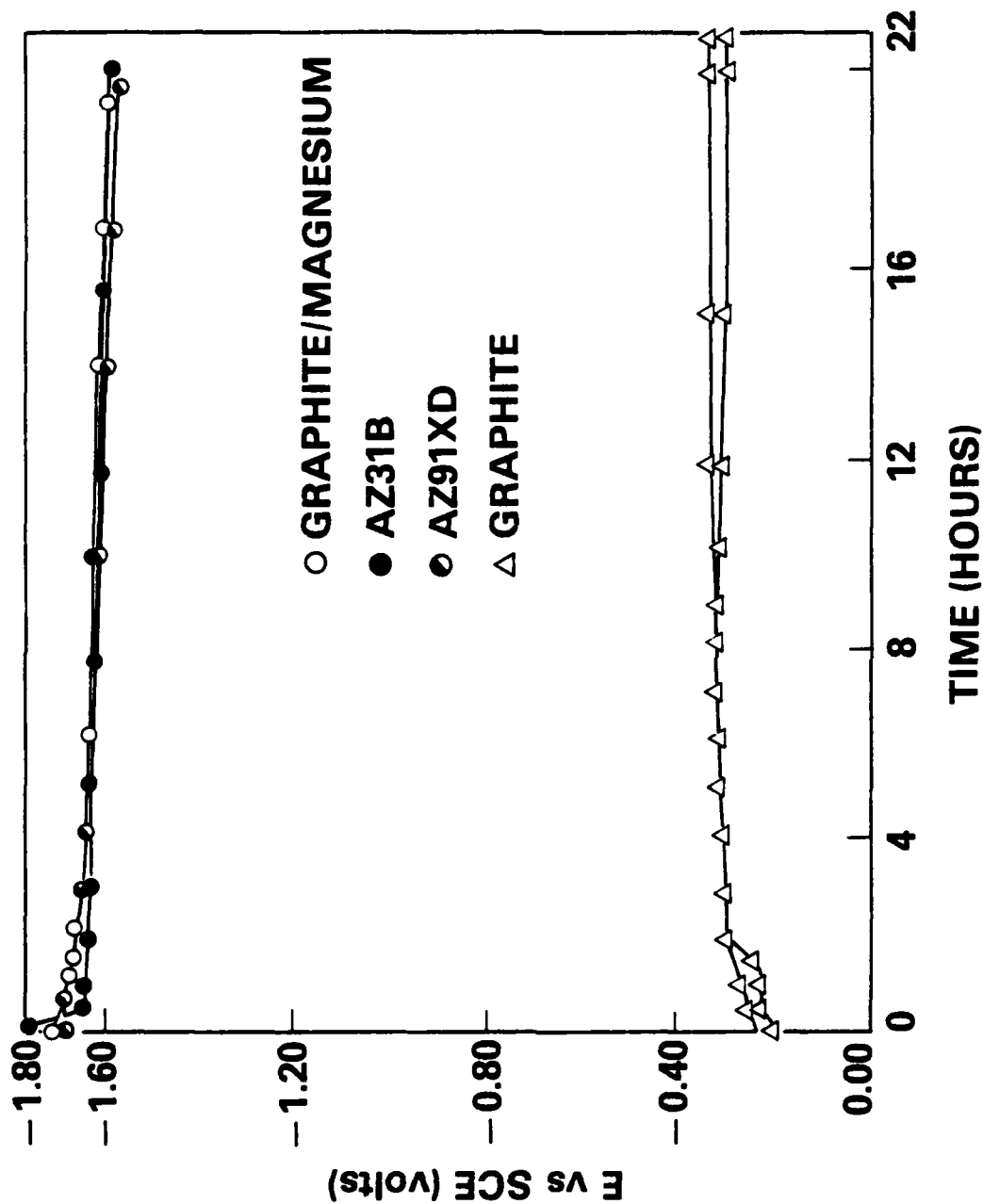


Fig. 7 — Open-circuit potentials of magnesium alloys AZ31B, AZ91XD, the graphite fiber/magnesium composite and graphite in boric acid buffer solution containing 1000 ppm NaCl.

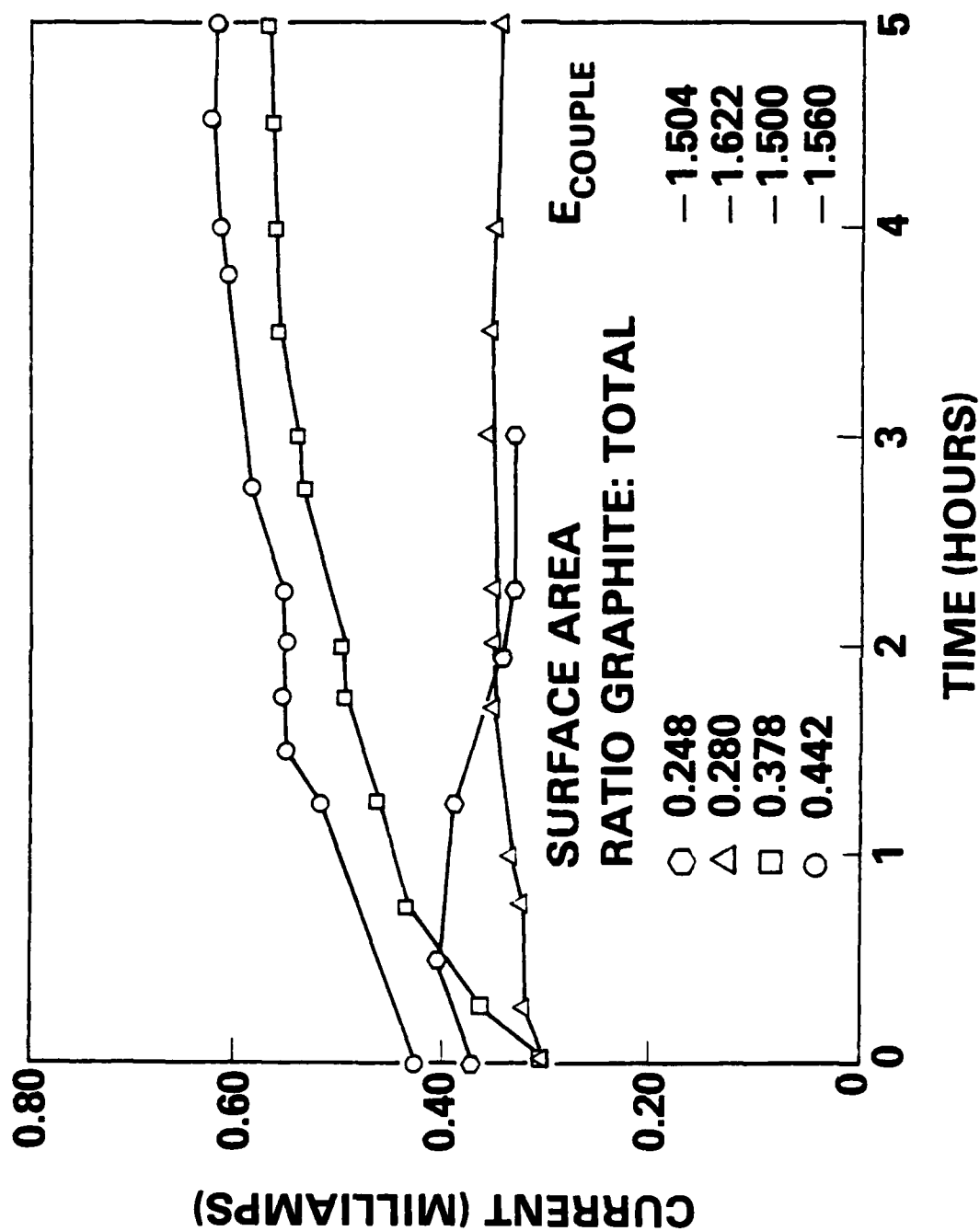


Fig. 8 — Short-circuit currents between AZ31B and graphite fibers for various surface area ratios of fiber in borated boric acid solution containing 1000 ppm NaCl.

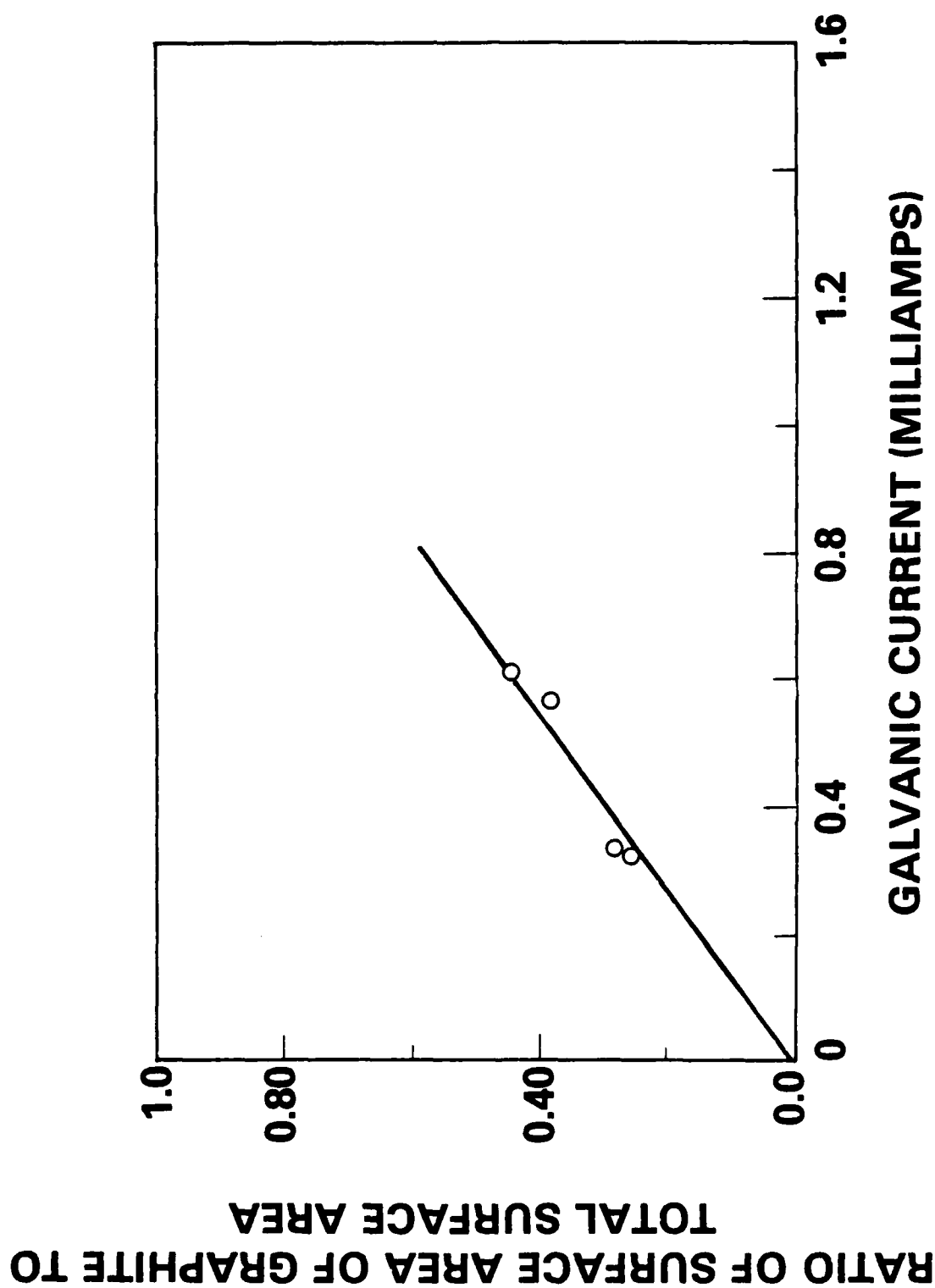


Fig. 9 — Galvanic currents of graphite-magnesium couples as a function of surface area ratio of graphite to total surface area for a borated boric acid solution containing 1000 ppm NaCl.

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